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# Preparation and characterization of electrolytic alumina deposit on austenitic stainless steel

S. El Hajjaji<sup>a,\*</sup>, M. El Alaoui<sup>a,b</sup>, P. Simon<sup>b</sup>, A. Guenbour<sup>a</sup>, A. Ben Bachir<sup>a</sup>,  
E. Puech-Costes<sup>c</sup>, M.-T. Maurette<sup>c</sup>, L. Aries<sup>b</sup>

<sup>a</sup>Laboratoire d'Electrochimie—Corrosion, Université Med V, Faculté des Sciences, Av Ibn Batouta, BP 1014 Rabat, Morocco

<sup>b</sup>CIRIMAT, LCMIE, Université Paul Sabatier, 118 Route de Narbonne, 31064 Toulouse Cedex 4, France

<sup>c</sup>IMRCP, Groupe POM, Université Paul Sabatier, 118 Route de Narbonne, 31064 Toulouse Cedex 4, France

## Abstract

Conversion coating modified by alumina has been studied as a way for improving the resistance to thermal oxidation of an austenitic stainless steel. Conversion coating, characterized by a particular morphology and strong interfacial adhesion with the substrate, facilitate the electrochemical deposition of ceramic layers and enhance their adhesion to the substrate. The influence of the current density and treatment time on alumina deposit was studied using statistical experimental designs like Doehlert uniform shell design. After heating, coatings present a continuous composition gradient with refractory compounds at the surface. The behavior at high temperature (1000 °C) of the alumina coating was investigated. The presence of alumina increases the oxidation resistance of an austenitic stainless steel at 1000 °C. The morphology and the chemical composition of the deposit are analyzed. Results on the thermal stability of coating on austenitic stainless steel are presented.

**Keywords:** Electrolytic deposit; Statistical experimental design; Surface analysis; Conversion coating; Alumina; Oxidation; Austenitic stainless steel

## 1. Introduction

Metals and alloys often have to be protected against oxidation at high temperatures. This is usually done by the use of ceramic oxides such as alumina [1–6]. Numerous methods can be used to obtain these coatings [1–12]. The most interesting ones is the electrochemical deposition which present several advantages [1–2,4,6,7].

In order to obtain a strongly adherent ceramic layer, an original method has been developed [2,7,13] which involves three steps. The first step consists of a controlled conversion treatment in acid solution, in order to functionalize the surface. The particular morphology of the conversion coating obtained present micropores and a high specific

area, which makes the surface suitable for the subsequent deposit.

In the second step, the ceramic layer is deposited by a cheap and easy electrochemical method which allows the control of the thickness, the morphology, and the composition of the coating, by varying the electrochemical parameters and bath composition.

In the third step, heating induces coat dehydration and leads to a reaction at the interface, between the conversion coating compounds and the electrochemical deposit, that improves coating adhesion.

The purpose of this paper is the study of alumina coating prepared by cathodic treatment of the functionalized austenitic stainless steel in an aqueous solution.

This study was undertaken to prepare and to investigate the composition, the morphology, and the thermal behavior of alumina coating. The parameters of alumina deposit have been studied using statistical experimental designs. The electrochemical process of deposit and the Doehlert shell design are briefly reviewed before the experimental results are presented.

\* Corresponding author. Tel./fax: +212 3777 5440.

E-mail addresses: selhajjaji@hotmail.com (S. El Hajjaji), hajjaji@fsr.ac.ma (S. El Hajjaji).

Table 1  
Chemical composition of austenitic stainless steel (wt%)

C	Cr	Ni	Mo	Cu	Si	S	Ti	Fe
0.031	18.20	10.30	0.10	0.06	0.77	0.007	0.01	Bal.

## 2. Experimental procedure

### 2.1. Preparation of conversion coating

Deposits were prepared on an austenitic stainless steel, its composition are given in Table 1. Substrates were prepared in the form of 0.5 mm×10 mm×10 mm specimens. Samples were cleaned with tetrahydrofurane (ACROS ORGANIC, purity=99%), washed with distilled water and then dried in air at room temperature.

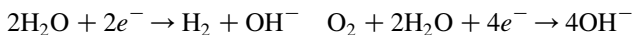
Stainless steel conversion coatings can be obtained either by electrolytic or chemical treatment in acid bath containing suitable additives and particularly substances containing chalcogenides such as sulphur (sulphides, thiosulphates) [13]. Corrosion inhibitors like acetylenic alcohols are also required to facilitate the control of film growth in order to obtain coats with specific proprieties [13].

In this study, the conversion treatment involved two steps: firstly the austenitic stainless steel was dipped in sulphuric acid solution at 20% (purity 98%) for 10 s and then was dipped in acid solution containing additives such as thiosulphate and propargyl alcohol, in order to control the growth of the coating and to obtain properties such as microporosity with the resulting high surface area. Conditions of the conversion treatment are presented in Table 2.

### 2.2. Preparation of alumina deposits

Secondly, the electrochemical deposition of alumina compounds was performed in aqueous solution using platinum electrode as anode and a saturated calomel electrode as reference (SCE).

The alumina deposit was induced by cathodic reactions, according to a process which involves both electrochemical and chemical reactions [13]. The cathodic reactions, with species such as protons and dissolved oxygen induces a local rise in pH at the electrode



The pH increase provokes precipitation in the pores and at the surface of oxides or hydroxides compounds with varying degrees of hydration [1,3]

Table 2  
Conditions of the conversion treatment

Acid bath	Hydrated sodium thiosulphate	Propargyl alcohol	Bath temperature (°C)	Treatment time (min)	Current (μA)
Sulphuric acid: 0.2%	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O: 2 g/L	C <sub>3</sub> H <sub>4</sub> O: 1.25 mL/L	55–60	20	300



In process optimization (or evaluation) there has always been a strong belief that to determine how one factor influences a response, all other factors must be held constant while only varying that particular factor. As a result, many investigations are still carried out using the inefficient ‘changing one separate factor at a time’. This approach might lead to incomplete mapping of the behavior of the system, often resulting in poor understanding, as well as incorrect conclusions. This approach is applicable only when there are no interactions among the studied factors. Interaction effects are measures of how the response *y* changes, with respect to a factor, as another factor changes. So, optimization benefit the use of statistical designs [14–16]. These are informationally optimal mathematical schemes in which all important factors are changed simultaneously, thereby facilitating the identification of process relations as well as the location of the real process optimum. In order to determinate the conditions of alumina deposit, we used a Doehlert uniform shell design. A full second-order polynomial empirical model is often sufficient for adequately describing an electrolytic alumina deposit process, at least in a selected limited experimental domain. This strategy allows an estimate (using the least squares law) to be made of the coefficients of a quadratic polynomial model (response *y* versus *X*<sub>1</sub> and *X*<sub>2</sub>). In the present work, two factors were studied, treatment time (*X*<sub>2</sub>) and current density (*X*<sub>1</sub>), requiring that six coefficients be determined as follows:

$$y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2$$

With this strategy, seven experiments were necessary and, in a coded space *X*<sub>1</sub>*X*<sub>2</sub>, were distributed as follows: six points were the vertices of a regular hexagon and the seventh one was its center [14,15]. The experimental design and the corresponding scheme are presented in Table 3 and Fig. 1. Their variation domains were determined in preliminary experiments (Table 4).

To minimize the effect of uncontrolled factors and time variations, all experiments were performed in random order and the calculation was obtained by the NEMROD program [16]. In order to show the effect of each factor, the studied response is the mass gain of alumina deposit.

Table 3  
Doehlert design: theoretical values of coded variables

Experiment no.	$X_1$	$X_2$
1	1	0.0
2	-1	0.0
3	0.5	0.866
4	-0.5	-0.866
5	0.5	-0.866
6	-0.5	0.866
7	0.0	0.0

The other conditions of deposits are presented in Table 5. After the preparation, samples were washed with water, dried in air at 70 °C and then heated at 900 °C for 2 h.

### 2.3. Characterization methods

The coatings were analyzed by secondary ions mass spectroscopy (SIMS) and the surface morphology was examined by scanning electron microscopy (SEM). Iso-thermal oxidation tests were performed on a TAG 24 SETARAM thermobalance. Oxidation kinetics of uncoated and coated samples were studied at temperature 1000 °C for 8 h in dynamic air at atmospheric pressure as a function of time. The total corrosion was evaluated by measuring the weight-gain as a function of heating time. The sensitivity, accuracy, and stability of the balance signal permitted a careful and accurate analysis of the oxidation kinetics.

## 3. Results and discussion

### 3.1. Morphology and chemical composition of conversion coating

Visually, the conversion coating appeared homogeneous. Examination by scanning electron microscopy (SEM) of the obtained conversion coating showed that the layer had a uniform appearance. The surface was rough which suggests that the conversion coating has a fractal character (Fig. 2).

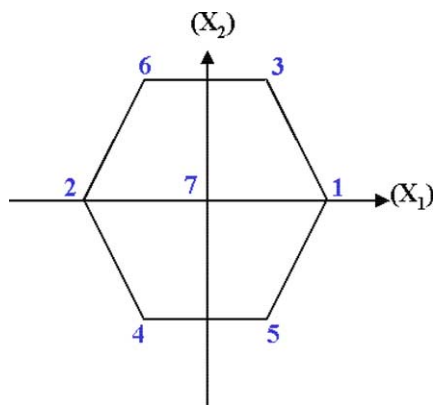


Fig. 1. Location of seven points of two-factor Doehlert uniform shell design in coded factor space.

Table 4  
Factors and their levels for the experiments

	$i$ (mA/cm <sup>2</sup> ) ( $X_1$ )	Treatment time (min) ( $X_2$ )
Level (-1)	-30	10
Level (+1)	-100	30

Table 5  
Conditions for the synthesis alumina films on austenitic stainless steel

Solution	Temperature (°C)	Agitation
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O: 1 mol/L	12	Yes

This specific morphology is well suitable to facilitate the deposition and the ‘anchoring’ of the alumina deposit.

Secondary ion mass spectroscopy analysis shows a concentration gradient of metallic elements in the coatings (Fig. 3). The coating is characterized by a continuous variation of the chemical composition from the metallic substrate to the superficial zone. SIMS profiles indicate that the surface contains only nickel compounds. Fe and Cr present identical profiles, which suggests that they are part of the same chemical compounds.

### 3.2. Preparation of alumina deposit

Aluminium hydroxide was deposited through cathodic reactions in aqueous solution of aluminium sulphate. In order to determine the electrolytic alumina deposit conditions, we have used Doehlert uniform shell design. Two variables studied were current density ( $X_1$ ) and treatment time ( $X_2$ ).

The experimental design according to Doehlert’s matrix and response values are given in Table 6. Processing of the data led to the estimation of six coefficients for the polynomial equation for response as follows:

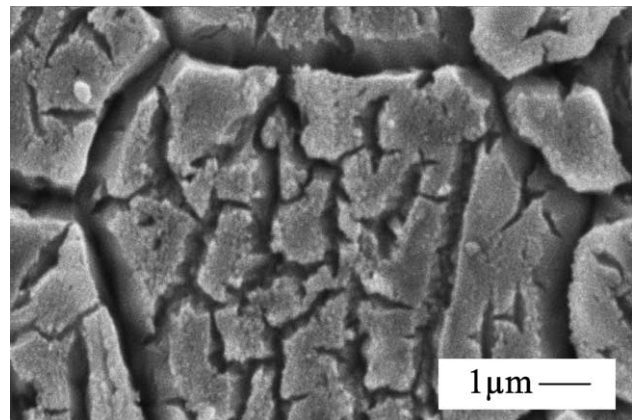


Fig. 2. SEM image of conversion coating on austenitic stainless steel.

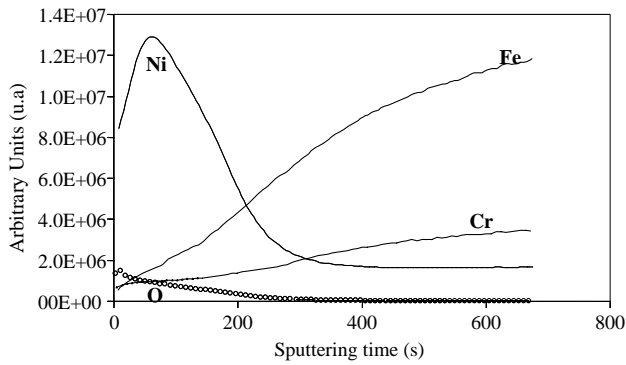


Fig. 3. Distribution profiles of elements in the conversion coating against bombardment time.

$$\Delta m = 1.183 + 0.102X_1 + 0.217X_2 - 0.11X_1X_1 \\ + 0.154X_2X_2 - 0.502X_1X_2$$

( $X_1$ : current density,  $X_2$ : treatment time)

Fig. 4 represents the variation of response  $\Delta m$  according to current density and treatment time. Results show that the increase in treatment time and the decrease in current density increase the mass gain of alumina deposit. The mathematical resolution for this equation led to an area where the mass gain of the alumina deposit is the highest. The high mass gain of alumina deposit has been obtained for the conditions given in Table 7.

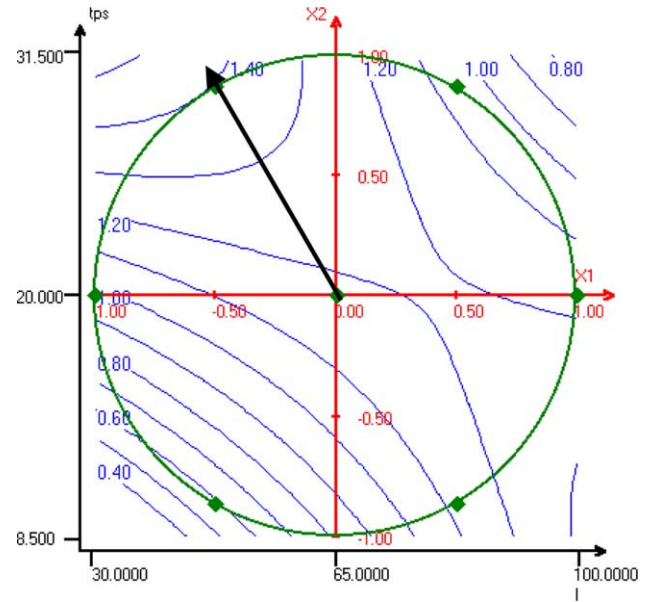
### 3.3. Morphology and chemical composition of the alumina deposit

After electrolytic preparation (before heating), visually, coatings appeared homogeneous. SEM examination showed that it was uniform. Alumina deposit presents the ‘cracked-mud’ morphology induced on drying the wet coating in air at 70 °C (Fig. 5).

SIMS profiles show a continuous concentration gradient of metallic elements in the coating from the metallic

Table 6  
Doehlert design: natural variables and result for each experiment

No.	$X_1$ , current density (mA/cm <sup>2</sup> )	$X_2$ , treatment time (min)	Mass gain, $\Delta m$ (mg/cm <sup>2</sup> )
1	−100	20	1.2
1	−100	20	1.1
2	−30	20	1.1
2'	−30	20	0.9
3	−82.5	30	1.1
3'	−82.5	30	1.03
4	−47.5	10	0.7
4'	−47.5	10	0.4
5	−82.5	10	1.1
5'	−82.5	10	1.2
6	−47.5	30	1.4
6'	−47.5	30	1.4
7	−65	20	1.2
7'	−65	20	1.1





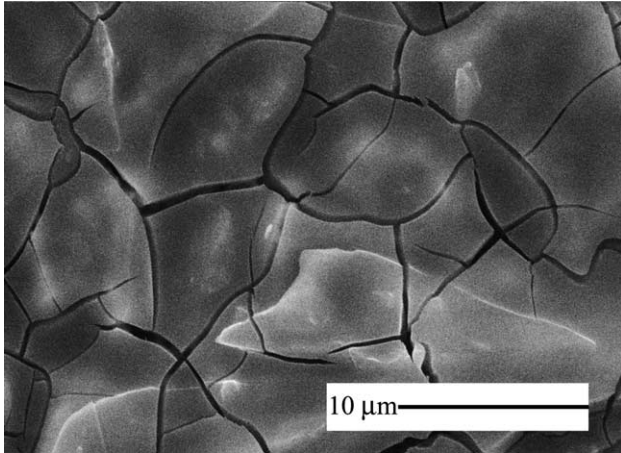


Fig. 5. SEM image of obtained alumina deposit on austenitic stainless steel.

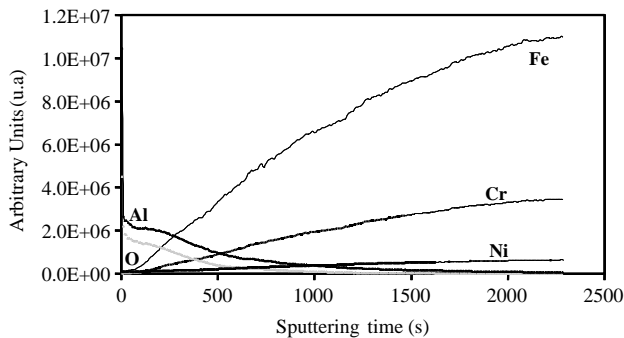


Fig. 6. Distribution profiles of elements in the obtained alumina deposit against bombardment time.

uncoated alloy, which can be attributed to the cracking or partial detachment of the oxide scale. For the uncoated alloy, the weight-gain increased with temperature and the oxidation is approximately linear.

After oxidation in air at 1000 °C, SEM observations of coated samples indicate that the surface does not present scale spalling phenomenon (Fig. 8). Heating induces an important modification of the initial coating morphology: it led to nodules forming a compact structure and the cracked mud aspect disappears. Treatment at high temperature

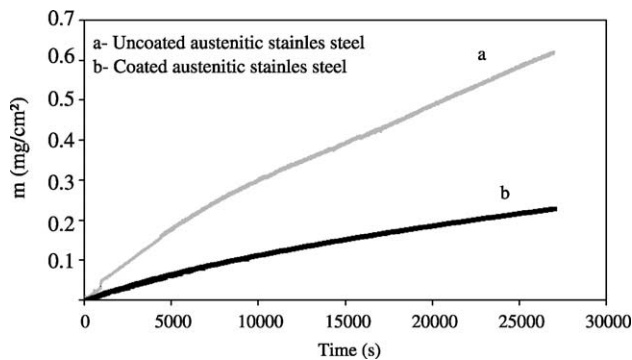


Fig. 7. Oxidation curves at 1000 °C in air for 8 h for uncoated and coated austenitic stainless steel.

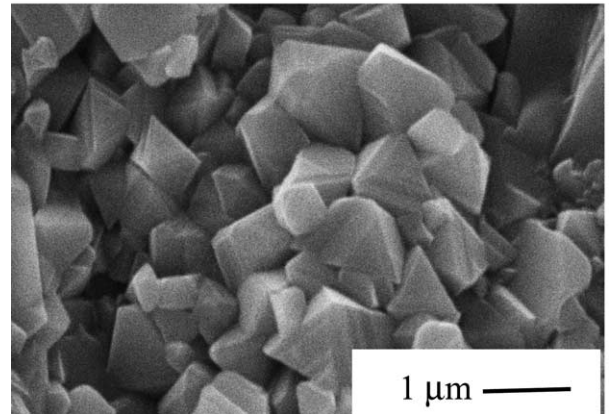
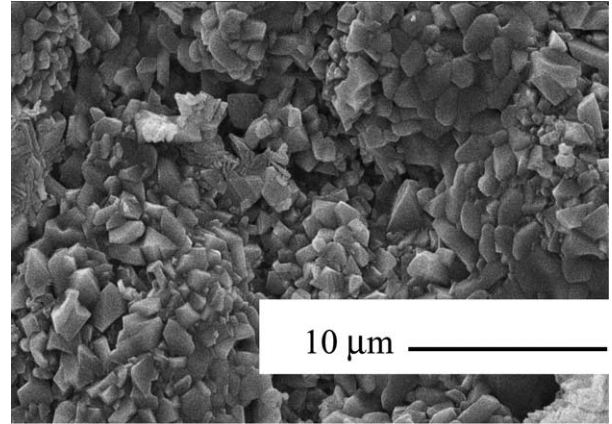


Fig. 8. SEM images of alumina coatings after oxidation at 1000 °C in air for 8 h.

induced crystallization phenomenon which led to small crystals of about 1 μm in size.

The X-ray diffraction spectrum of the oxidized coated steel show the peaks corresponding to  $\alpha$  alumina, mixed iron–chromium oxide and smaller peaks of nickel oxide.

#### 4. Conclusion

The subject of this paper was the preparation and the characterization of electrolytic alumina coating on an iron–chromium–nickel alloy. The method involves a cathodic treatment of the samples in a solution containing aluminum salts; the austenitic stainless steel must be initially functionalized by a suitable conversion treatment. In this paper, alumina coating process has been studied by statistical experimental design; the increase of treatment time and the decrease of current density increase the mass gain of alumina deposit. Observations and analysis, respectively, by SEM and SIMS of the alumina coating show that the surface was uniform and the profiles were continuous. The study of thermal behavior of this coated austenitic stainless steel at 1000 °C shows that the alumina has a protector character at high temperature. The low oxidation rate is due to the presence of  $\alpha$  alumina which

reinforces the protector character of mixed iron–chromium oxide.

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### References

- [1] R. Chaim, I. Silberman, L. Gal-Or, J. Electrochem. Soc. 138 (1991) 1942–1946.
- [2] L. Aries, L. Alberich, J. Roy, J. Sotoul, Electrochem. Acta 41 (18) (1996) 2799–2803.
- [3] L. Gal-Or, I. Silberman, R. Chaim, J. Electrochem. Soc. 138 (1991) 1939–1942.
- [4] R. Chaim, G. Stark, L. Gal-Or, H. Bestgen, J. Mater. Sci. 29 (1994) 6241–6248.
- [5] H. Honno, M. Tokita, A. Furusaki, R. Furuichi, Electrochem. Acta 37 (1992) 2421–2425.
- [6] D. Trench, L. Warren, J. Electrochem. Soc. 130 (1983) 869–872.
- [7] L. Aries, J. Roy, J. Sotoul, V. Pontet, P. Costeseque, T. Aigouy, J. Appl. Electrochem. 26 (1996) 617–622.
- [8] S. El Hajjaji, A. Ben Bachir, L. Aries, Surf. Eng. 17 (2001) 201–204.
- [9] S. El Hajjaji, S. Manov, J. Roy, T. Aigouy, A. Ben Bachir, L. Aries, Appl. Surf. Sci. 180 (2001) 293–301.
- [10] S. El Hajjaji, A. Guenbour, A. Ben Bachir, L. Aries, Corros. Sci. 42 (2000) 941–956.
- [11] L. Aries, J. Roy, F. Senocq, S. El Hajjaji, Mater. Corros. 51 (2000) 496–501.
- [12] S. El Hajjaji, M.-T. Maurette, E. Puech-Costes, A. Ben Bachir, L. Aries, Br. Corros. J. 34 (1999) 273–279.
- [13] L. Aries, J. Appl. Electrochem. 24 (1994) 554–558.
- [14] D.H. Doehlert, Appl. Stat. 19 (1970) 231–241.
- [15] D.H. Doehlert, V.L. Klee, Discrete Math. 2 (1972) 309–319.
- [16] D. Mathieu, R. Phan-Tan-Luu, NEMROD<sup>®</sup> Software, LPRAI, Marseille, France, 1995.